



Short communication

Cyclic voltammetric study of arsenic reduction and oxidation in hydrochloric acid using a Pt RDE

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1. Introduction

High levels of arsenic in groundwater pose threats to both wildlife and humans. The causes can be natural geological processes such as soil erosion and leaching or human activities like disposal of industrial wastewater, mining and use of agricultural chemicals. Arsenic exists in the natural environment mainly in the forms of arsenite (As(III)) and arsenate (As(V)). Arsenite is more toxic [1] and mobile than arsenate [2]. Arsenic species can be removed from water by goethite or iron oxyhydroxide [3–5], precipitative softening [6], activated alumina [7] and flotation [8, Pan et al. submitted for publication]. Recent studies have shown that zero-valent iron powder is effective in arsenic removal [9, 10]. The mechanism was proposed to be surface precipitation of arsenic on iron [9]. It is also possible that arsenic is reduced on the surface of iron and Fe–As amalgam is formed. Therefore, the study of reduction of arsenic to its elemental form is of both theoretical and practical importance.

In addition, for the analysis of arsenic concentration and speciation [11], a non-interfering means of oxidizing arsenite to arsenate is desired. Electrochemical oxidation, which does not involve any use of chemicals, is environmentally favorable and causes no interference in colorimetric measurements. Achieving better oxidation efficiency using electrochemical methods requires understanding of the redox mechanism of arsenic species in aqueous solution. Cyclic voltammetry (CV) is a powerful technique for the investigation of redox reactions in aqueous solution, surface deposition and adsorption [12, 13]. When combined with a rotating disk electrode (RDE), it can also shed light on reaction kinetics [14, 15]. With better understanding of the redox reactions between arsenic species, the reactions can be controlled either chemically or electrochemically, to achieve desired effects such as high conversion rate of arsenite to arsenate in arsenic removal by adsorption.

2. Experimental details

2.1. Solutions

All experiments were carried out in 1 g l⁻¹ As(III) + 1 g l⁻¹ As(V) + 1 M HCl solution, which was prepared by dissolving arsenic(III) oxide (Aldrich, 99.995%) and arsenic(V) oxide (Aldrich, 99.99 + %) in 1 M hydrochloric acid (Amend). The oxidation state of the samples was not confirmed in the laboratory. Both arsenite and arsenate were present in the testing solution to ensure the observation of all possible redox reactions between arsenic species. Water used was triply distilled. All chemicals were used as received without further purification.

2.2. Electrochemical measurements and instrumentation

A three-electrode system was employed. The working electrode was a Pt RDE (Pine) with an exposed area of 0.5 cm² mounted to a Pine rotator. A coiled platinum wire (Alfa Aesar, 99%) was the counter electrode and a saturated calomel electrode (SCE) (Fisher) as the reference electrode. RDE and platinum wire were stored in 1 M H₂SO₄ solution and washed with distilled water thoroughly before use. A potentiostat (PAR M 173) together with a signal generator (PAR M 175) controlled the potential of the working electrode. The current was measured by a built-in ammeter (PAR M 179) and recorded by a computer. Solutions were purged with high purity nitrogen gas (T.W. Smith) before experiment. All experiments were performed at room temperature (24 ± 2 °C). All potentials are reported relative to SCE.

3. Results and discussion

Representative cyclic voltammograms of Pt RDE in 1 g l⁻¹ As(III) + 1 g l⁻¹ As(V) + 1 M HCl solution

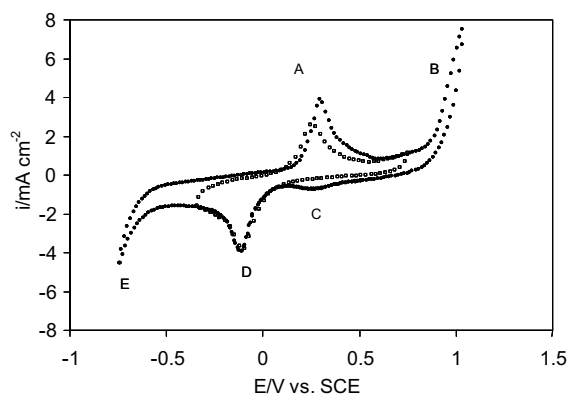
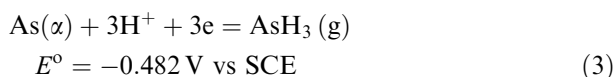
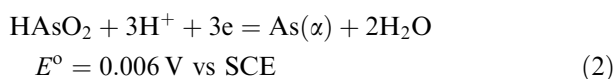
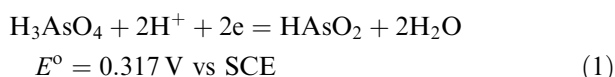


Fig. 1. Cyclic voltammograms of Pt RDE in 1 g l⁻¹ As(III) + 1 g l⁻¹ As(V) + 1 M HCl. Electrode rotation speed = 1000 rpm; ν = 500 mV s⁻¹. □ □ □ potential range: -0.75–1.00 V vs SCE, □ □ □ potential range: -0.35–0.75 V vs SCE.

over a wide potential range are shown in Figure 1. One distinct anodic peak (A) and one distinct cathodic peak (D) were observed at 0.3 and -0.12 V, respectively, on the curve obtained at wider potential range. A small, broad cathodic peak (C) was also detected at 0.24 V. There was large anodic current (B) at potentials more positive than 1.0 V and large cathodic current (E) at potentials more negative than -0.5 V. On the other hand, on the curve acquired with a narrower potential scan, the small cathodic peak disappears while the distinctive cathodic and anode peaks remain.

Under the testing conditions, the stable forms of arsenite and arsenate are HAsO₂ and H₃AsO₄, respectively [16]. Possible associating reactions and their standard reversible potentials are [17]:



Therefore, the anodic peak (A) may represent oxidation of arsenite to arsenate or of elemental arsenic to arsenite; the cathodic peak (D), correspondingly, may stand for reduction from arsenate to arsenite or from

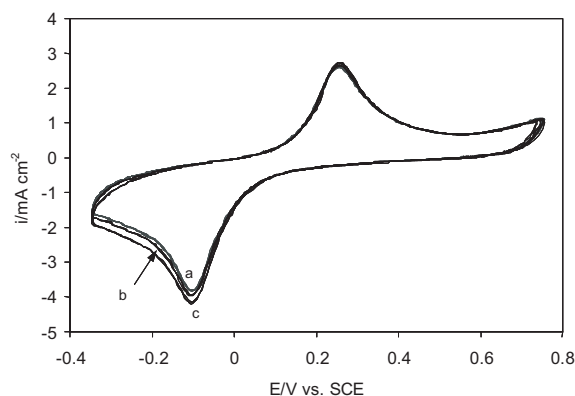


Fig. 2. Cyclic voltammograms of Pt RDE in 1 g l⁻¹ As(III) + 1 g l⁻¹ As(V) + 1 M HCl. ν = 500 mV s⁻¹, electrode rotation speed = (a) 1000 rpm, (b) 1600 rpm and (c) 3600 rpm.

arsenite to elemental arsenic. The large anodic current (B) may be the combined result of oxygen evolution and the formation of surface platinum oxide [18, 19]. The large cathodic current (E) is due to the evolution of hydrogen and possibly arsine gas. The small cathodic peak (C), which does not appear when the potential does not go beyond 0.75 V is most likely due to the reduction of surface oxide formed during the potential scan at $E > 0.8$ V.

Cyclic voltammograms of Pt RDE in arsenic solutions at different electrode rotation speeds are shown in Figure 2. The peak potential and current densities are listed in Table 1. For a RDE, the diffusion layer thickness, δ , is related to the rotation speed of the electrode by the following equation

$$\delta = 1.62 D^{1/3} \omega^{-1/2} \nu^{1/6} \quad (4)$$

where D is the diffusion coefficient of the species, T is the angular velocity of the electrode and Λ is the kinematic viscosity of the solution. If a reaction is controlled by diffusion of species to and from the electrode interface, then the peak current should increase proportionally to the square root of the rotation speed of the RDE. The experimental results, however, show that both the anodic and cathodic peak current densities do not change significantly with rotation speed, suggesting that both reactions are controlled by surface processes rather than by ion transportation. Of the two possible reactions assigned for peaks (A) and (D), the redox reactions between arsenite and arsenate are apparently more

Table 1. Observed cathodic peak potentials (E_{pc}), cathodic peak current densities (i_{pc}), anodic peak potentials (E_{pa}) and anodic peak current densities (i_{pa}) from Pt RDE voltammograms in 1 g l⁻¹ As(III) + 1 g l⁻¹ As(V) + 1 M HCl at different electrode rotation speeds

Rotation Speed/rpm	E_{pc} /V vs SCE	i_{pc} /mA cm ⁻²	E_{pa} /V vs SCE	i_{pa} /mA cm ⁻²
1000	-0.104	-3.20	0.256	2.25
1600	-0.104	-3.34	0.256	2.33
3600	-0.104	-3.58	0.256	2.40

$$\nu = 500 \text{ mV s}^{-1}$$

Table 2. Observed cathodic peak potentials (E_{pc}), cathodic peak current densities (i_{pc}), anodic peak potentials (E_{pa}) and anodic peak current densities (i_{pa}) from Pt RDE voltammograms in $1 \text{ g l}^{-1} \text{ As(III)} + 1 \text{ g l}^{-1} \text{ As(V)} + 1 \text{ M HCl}$ at different potential scan rates

$v/\text{mV s}^{-1}$	E_{pc} /V vs SCE	i_{pc} /mA cm $^{-2}$	$i_{pc} v^{-1/2}$ /mA cm $^{-2} \text{ mV}^{-1/2} \text{ s}^{1/2}$	E_{pa} /V vs SCE	i_{pa} /mA cm $^{-2}$	$i_{pa} v^{-1/2}$ /mA cm $^{-2} \text{ mV}^{-1/2} \text{ s}^{1/2}$
50	-0.078	-0.85	-0.12	0.239	0.45	0.063
100	-0.083	-1.00	-0.10	0.239	0.70	0.070
200	-0.094	-1.70	-0.12	0.248	1.18	0.083
500	-0.104	-3.20	-0.14	0.256	2.25	0.10
900	-0.117	-4.70	-0.16	0.272	3.76	0.12

Electrode rotation speed = 1000 rpm

dependent on ion transport than those between arsenite and elemental arsenic. Therefore, the cathodic peak (A) and the anodic peak (D) more likely represent the redox reactions between elemental arsenic and arsenite. This result is in agreement with the study of arsenic redox reactions on Pt RDE in perchloric acid [20] and that on gold in perchloric acid with potassium chloride solutions [21]. However, the anodic peak of arsenite oxidation, which was observed clearly in perchloric acid on Pt RDE [20], was not evident in this study.

The cyclic voltammograms of Pt RDE in arsenic solutions at different potential scan rates are shown in Figure 3. The corresponding peak potential and current densities are given in Table 2. The peak potentials changes with increasing scan rate and the peak potential difference is as large as 300 mV, all pointing to the irreversibility of the redox reactions between arsenite and elemental arsenic and a small exchange current density. The products of peak current density and reverse square root of potential scan rate are also given in Table 2. The product increases with potential scan rate. For a simple irreversible electron transfer reaction, the product should remain constant. The changing product suggests a complex set of mechanisms for the redox reaction.

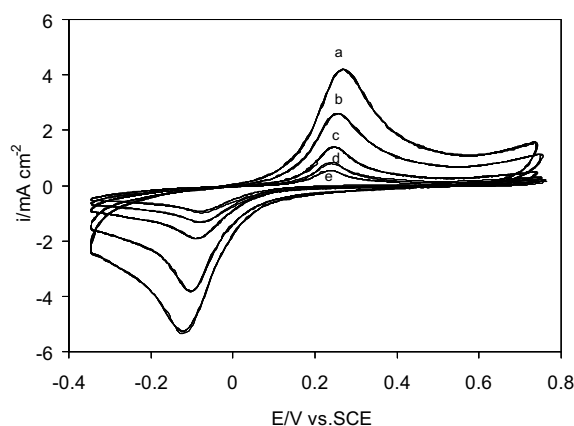


Fig. 3. Cyclic voltammograms of Pt RDE in $1 \text{ g l}^{-1} \text{ As(III)} + 1 \text{ g l}^{-1} \text{ As(V)} + 1 \text{ M HCl}$. Electrode rotation speed = 1000 rpm; v = (a) 900 mV s^{-1} , (b) 500 mV s^{-1} , (c) 200 mV s^{-1} , (d) 100 mV s^{-1} and (e) 50 mV s^{-1} .

4. Summary

The redox reactions of arsenic species in hydrochloric acid was studied by CV with a Pt RDE at different potential scan rates and electrode rotation speeds. Distinct current peaks associated with redox reactions between arsenite and elemental arsenic were observed, while no peak related to the oxidation of arsenite to arsenate or the reduction of elemental arsenic to arsine was observed. The redox reactions between arsenite and elemental arsenic were determined to be irreversible and were shown to involve complex reaction mechanisms. The observation of elemental arsenic reduction on Pt in aqueous solutions suggests that the removal of arsenic by zero-valent iron possibly involves the reduction of arsenite; the absence of redox peaks between arsenite and arsenate indicates that it is difficult to control the speciation between As(III) and As(V) electrochemically.

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References

1. J.F. Ferguson and J. Gavis, *Water Res.* **6** (1972) 1259.
2. L.E. Deuel and A.R. Swoboda, *J. Environ. Qual.* **1** (1972) 317.
3. M.L. Pierce and C.B. Moore, *Environ. Sci. Technol.* **14** (1980) 214.
4. S. Fendof, M.J. Eick, P. Grossl and D.L. Sparks, *Environ. Sci. Technol.* **31** (1997) 315.
5. K.P. Raven, A. Jain and R.H. Loeppert, *Environ. Sci. Technol.* **32** (1998) 344.
6. L.S. McNeill and M. Edwards, *J. Environ. Eng.* **123** (1997) 453.
7. T. Lin and J. Wu, *Wat. Res.* **35**, (2001) 2049.
8. Y. Zhao, A.I. Zouboulis and K.A. Matis, *Separ. Sci. Technol.* **31** (1996) 769.
9. J.A. Lackovic, N.P. Nikolaidis and G.M. Dobbs, *Environ. Eng. Sci.* **17** (2000) 29.
10. J. Farrell, J. Wang, F. O'Day and M. Conklin, *Environ. Sci. Technol.* **35** (2001) 2026.

11. M.S. Edwards, S. Patel, L. MacNeil, H. Chen, M. Frey, A.D. Eaton, R.C. Antweiler and H.E. Taylor, *J. AWWA* **90** (1998) 103.
12. K. Polat, M.L. Aksu and A.T. Pekel, *J. Appl. Electrochem.* **32** (2002) 217.
13. R. Wartena, J. Winnick and P.H. Pfromm, *J. Appl. Electrochem.* **32** (2002) 725.
14. A. Neville, *J. Appl. Electrochem.* **29** (2002) 455.
15. J.M. Maciel, *J. Appl. Electrochem.* **30** (2002) 981.
16. M. Pourbaix, 'Atlas of Electrochemical Equilibrium in Aqueous Solutions', (Oxford, 1966), p. 516.
17. A.J. Bard, 'Encyclopedia of Electrochemistry of the Elements', Vol. 2, (Marcel Dekker), p. 23.
18. K.J. Vetter and J.W. Schultze, *J. Electroanal. Chem.* **34** (1972) 141.
19. H. Angerstein-Kozłowska, B.E. Conway and W.B.A. Sharp, *J. Electroanal. Chem.* **43** (1973) 9.
20. T.D. Cabelka, D.S. Austin and D.C. Johnson, *J. Electrochem. Soc.* **131** (1984) 1595.
21. P. Kedzierzawski and Z. Szklarska-Smialowska, *J. Electroanal. Chem.* **122** (1981) 269.